DEGRADATION OF HIGH DENSITY POLYETHYLENE CONTAINING MANGANESE CARBOXYLATES AS PRO-DEGRADANT ADDITIVES UNDER ARTIFICIAL AND NATURAL WEATHERING

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ABSTRACT

The tremendous utilization of synthetic plastics over last decades has led to environmental problems due to lack of degradability of plastics. The degradability issue has resulted in development of degradable plastics which degrade faster. This study deals with utilization of manganese carboxylates (i.e. manganese laurate, manganese palmitate and manganese stearate) on enhancing degradation of high density polyethylene (HDPE). Initially, manganese carboxylates were synthesized through two-steps reactions: (i) sodium carboxylates synthesis by reacting sodium hydroxide and carboxylic acids, (ii) manganese carboxylates synthesis by reacting manganese chloride and sodium carboxylates. Characterization of manganese carboxylates was then carried out. Incorporation of manganese carboxylates up to 1% (w/w) into HDPE resin was carried out using twin screw extruder followed by injection molding to produce specimens. Thermal treatment was performed at 70°C for maximum duration of 1000 hours to examine the degradation of pure HDPE and HDPE containing manganese carboxylates. Accelerated weathering was conducted up to 1000 hours combining thermal and UV exposure. Natural weathering was carried out for 24 weeks under weather conditions of Gambang, Malaysia. Analyses of tensile strength, elongation at break, FTIR spectra, average molecular weight, melt flow index (MFI), thermogravimetry (TG), differential scanning calorimetry (DSC), X-ray diffraction (XRD), and scanning electron microscopy (SEM) were carried out to asses the changes during treatments. Results have revealed that all manganese carboxylates have demonstrated adequate thermal stability. Their melting temperatures are in range of 108-117 °C. Manganese stearate has shown the highest thermal stability and melting point among manganese carboxylates synthesized. Thermal treatment has led to thermo-oxidative degradation of HDPE. Manganese carboxylates have significantly played a role in enhancing degradation of HDPE. The degradation increased by increasing amount of manganese carboxylates. During accelerated weathering, the degradation took place more rapidly than during thermal treatment, particularly for HDPE containing manganese carboxylates. Photo-degradation and thermo-oxidative degradation took place simultaneously during accelerated weathering and allowed dramatic reductions of essential properties. Natural weathering has given similar effects with accelerated weathering. Manganese carboxylates has also shown the capabilities on enhancing degradation of HDPE in natural environment. Manganese stearate has shown a slightly greater effect in enhancing degradation of HDPE than manganese laurate and manganese palmitate during all treatments. Pure HDPE lost its elongation at break about 16 %; 65 % and 64 %, whereas HDPE containing 1% manganese stearate lost its elongation at break about 62 %; 96 % and 95 % for thermal treatment; accelerated weathering and natural weathering respectively. Tensile strength and tensile modulus also decreased proportionally with the decrease of elongation at break. Other properties have also been found to decrease including average molecular weight, thermal stability, and melting point. The MFI, carbonyl index and crystallinity were found to increase after all treatments. Generally, manganese carboxylates have demonstrated the capabilities on enhancing degradation of HDPE under all modes of treatments.

ABSTRAK

Penggunaan bahan plastik yang banyak sejak beberapa dekad yang lalu membawa kepada masalah alam sekitar yang disebabkan oleh kekurangan sifat keteruraian bahan plastik. Isu keteruraian bahan plastik telah memberi kesan dalam pembaharuan penghasilan plastik yang lebih cepat terurai. Kajian ini melibatkan penggunaan mangan karboksilat (mangan laurat, mangan palmitat and mangan stearat) dalam meningkatkan penguraian polietilena ketumpatan tinggi (HDPE). Mangan karboksilat dihasilkan melalui dua kaedah tindakbalas: (i) natrium karboksilat disintesiskan melalui tindakbalas natrium hidroksida dengan asid karboksilik, (ii) mangan karboksilat disintesiskan melalui tindakbalas mangan klorida dengan natrium karboksilat. Pencirian mangan karboksilat kemudiannya dapat dihasilkan. Gabungan mangan karboksilat sehingga 1% (w/w) ke dalam HDPE resin telah dijalankan dengan menggunakan mesin pengekstrud skru berkembar yang kemudiannya melalui suntikan acuan untuk menghasilkan spesimen. Rawatan terma dilakukan pada suhu 70°C dengan masa maksima iaitu selama 1000 jam dalam menguji tahap penguraian HDPE tulen dan HDPE yang mengandungi mangan karboksilat. Pecutan pencuacaan dijalankan sehingga 1000 jam yang menggabungkan pendedahan terhadap terma dan cahaya sinar UV. Pencuacaan semulajadi dilakukan selama 24 minggu dengan keadaan cuaca di kawasan Gambang, Malaysia. Analisa kekuatan tensil, pemanjangan pada takat putus, spektrum FTIR, purata berat molekul, indeks aliran leburan(MFI), termogravimetri(TG), pembezaan imbasan kalorimetri(DSC), pembelauan sinar-X(XRD), imbasan mikroskop elektron(SEM) telah dijalankan untuk menilai perubahan yang berlaku semasa perawatan. Hasil ujikaji telah mendedahkan semua mangan karboksilat menunjukkan kestabilan terma yang mencukupi. Suhu lebur bagi mangan karboksilat tersebut dalam lingkungan 108-117°C. Mangan stearat menunjukkan kestabilan terma yang tertinggi dan takat lebur di antara mangan karboksilat sintesis yang lain-lain. Rawatan terma telah menyebabkan penguraian oksidatif terma bagi HDPE. Mangan karboksilat merupakan bahan penting dalam meningkatkan tahap penguraian HDPE. Penguraian akan bertambah dengan pertambahan kuantiti bahan mangan karboksilat. Semasa pencuacaan pecutan, penguraian berlaku dengan lebih cepat berbanding semasa perawatan terma, terutama bagi HDPE yang mengandungi bahan mangan karboksilat. Penguraian foto dan penguraian oksidatif terma berlaku secara serentak semasa pencuacaan pecutan dan membenarkan berlakunya kerencatan pada sifat-sifat penting secara dramatik. Pencuacaan semulajadi memberikan kesan serupa dengan pencuacaan pecutan. Mangan karboksilat juga menunjukkan kebolehupayaan dalam meningkatkan tahap penguraian HDPE di persekitaran semulajadi. Mangan stearat menunjukkan kesan yang lebih baik dalam meningkatkan tahap penguraian berbanding mangan laurat dan mangan palmitat dalam semua perawatan. HDPE tulen kehilangan pemanjangan pada takat putus iaitu 16%, 65% dan 64% sedangkan HDPE yang mengandungi mangan stearat kehilangan pemanjangan pada takat putus iaitu 65%, 96%, dan 95% bagi perawatan terma, pecutan pencuacaan dan pencuacaan semulajadi. Kekuatan tensil dan modulus tensil juga menurun secara berkadaran dengan penurunan pemanjangan pada takat putus. Sifat- sifat lain juga didapati merosot termasuk purata berat molekul, kestabilan terma dan takat lebur. Nilai MFI, indek karbonil dan sifat penkristalan didapati ada peningkatan dalam semua perawatan. Secara umumnya, mangan karboksilat telah menunjukkan keupayaan dalam meningkatkan penguraian HDPE dalam semua kedah perawatan.

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C	Concentration
Ea	Activation energy, kJ/mol
M_v	Average molecular weight
M_n	Number average
M_w	Weight average
$[\eta]$	Intrinsic viscosity
η_{sp}	Specific viscosity
η_{rel}	Relative viscosity
T_m	Melting temperature, °C
T_g	Glass transition temperature, °C
λ	Wave length of X-ray
d	Interplanar spacing of crystalline material
θ	Diffarction angle
ΔH_f	Heat of fusion, J/g
X_{DSC}	Crystallinity index obtained from DSC scan, %
X_{XRD}	Crystallinity index obtained from XRD trace, %

LIST OF ABBREVIATION

ASTM	American Society for Testing and Materials
ATR	Attenuated total reflectance
COC	Cyclic olefin copolymer
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
DTG	Differential thermogravimetry
FTIR	Fourier transform infrared
GPC	Gel Permeation Chromatography
HDPE	High density polyethylene
IR	Infrared
LDPE	Low density polyethylene
LLDPE	Linear low density polyethylene
MFI	Melt Flow Index
ML	Manganese laurate
MP	Manganese palmitate
MS	Manganese stearate
MW	Molecular weight
MWD	Molecular weight distribution
PC	Polycarbonate
PE	Polyethylene
PMMA	Polymethyl methacrylate
PS	Polystyrene
PVC	Polyvinyl chloride
SAN	Styrene acrylonitrile
SEC	Size exclusion chromatograpgy
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
TG	Thermogravimetry
XRD	X-ray difraction

CHAPTER 1

INTRODUCTION

1.1 RESEARCH BACKGROUND

Plastics have achieved almost irreplaceable role in many applications. Almost all aspects of life rely on the plastics. Recently, the usage of plastics increases significantly. Plastics have achieved an irreplaceable position in the packaging industry (Roy et al., 2006a). People rely to plastics in everyday activities, such as jugs, clothes, computer, etc (Bajer et al., 2007; Lokensgard, 2004). Plastics production systematically increases, thus, also amount of plastics waste grows (Bajer et al., 2007).

The world's annual production of polymer resins has experienced a steady growth since the beginning of the century, with growth predicted way into the 21st century. In developed countries, the growth in annual polymer production has diminished somewhat in recent years. However, developing countries in South America and Asia are now starting to experience tremendous growth (Osswald and Menges, 2003). From 2009 to 2010 the global plastics production increased by 15 million tonnes (6%) to 265 million tonnes, confirming the long term trend of plastics production growth of almost 5% per year over the past 20 years. Meanwhile in 2010 Europe accounted for 57 million tonnes (21.5%) of the global production and China overtook Europe as the biggest production region at 23.5% which mainly consisted of HDPE (11%), LDPE-LLDPE (17%), PP (18%) and PVC (8%). Figure 1.1 shows the growth of world plastics production from 1950-2010(PlasticsEurope, 2011).

There are over 18,000 different grades of polymers, available in the US alone. They can be divided into two general categories, thermosetting and thermoplastic polymers. In 1993, 90% of polymers produced in the United States were thermoplastics.

However, in a 1995 worldwide projection, thermoplastics account for 83% of the total polymer production (Osswald et al., 2006).

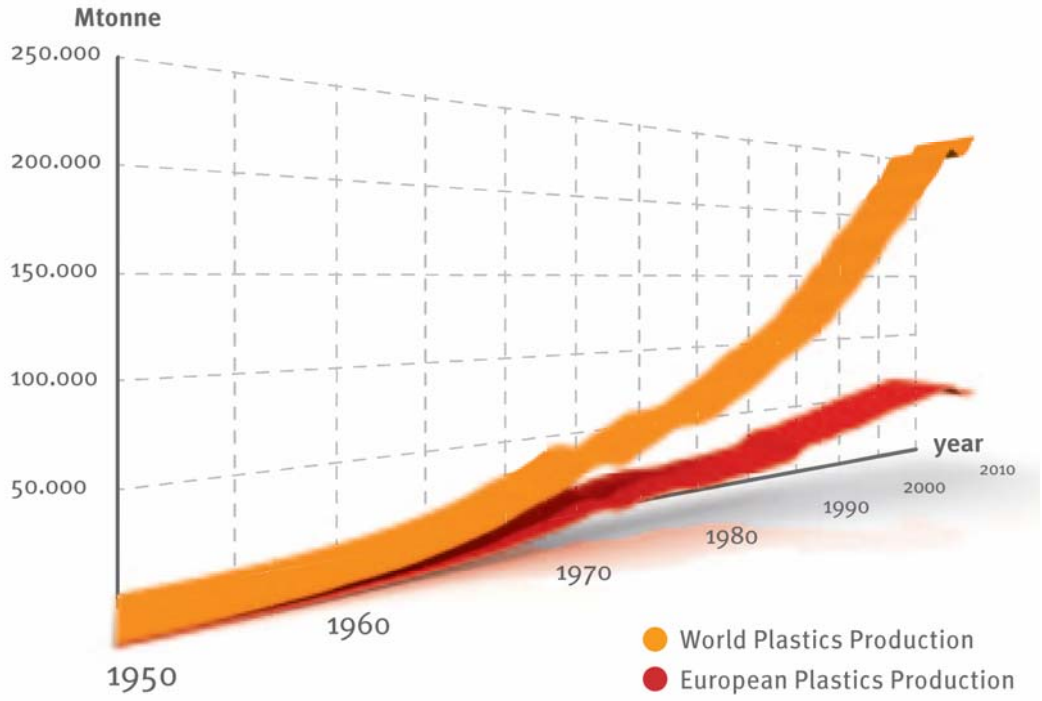
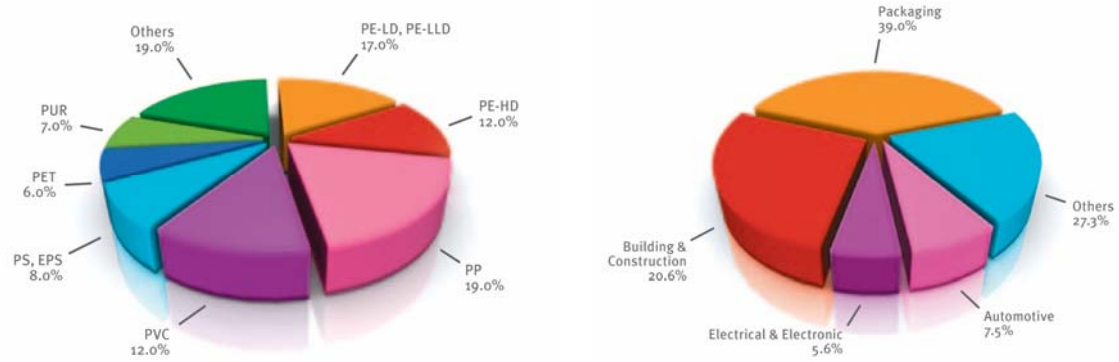


Figure 1.1 World plastics production 1950-2010 (PlasticsEurope, 2011)



(a) **(b)**

Figure 1.2 Plastics demand by converters 2010 in Europe: (a) breakdown by resin types, (b) breakdown by end use segments

There are five high-volume plastics families; polyethylene (including low density (LDPE), linear low density (LLDPE) and high density (HDPE)), polypropylene (PP), polyvinylchloride (PVC), polystyrene (solid PS and expandable EPS) and

polyethylene terephthalate (PET). Figure 1.2 shows plastics demand in Europe in 2010(PlasticsEurope, 2011). Other data revealed that in 1999, the principal thermoplastic polymers (LDPE/HDPE, PP, PVC, PS, and PET) consumptions exceeded 28 millions tons in Western Europe, 79% of total plastic markets (thermoplastics and thermosets) in Western Europe and around 90% of total thermoplastics markets (Azapagic et al., 2003). In 2010 together the big five accounted for around 74% of all European plastics demands (PlasticsEurope, 2011).

In 2009 the total consumption of plastics resin in Malaysia accounted for 1.70 million metric tons (MT)(Boon, 2010). Previously total resin consumption accounted for 1.72 million MT in 2005, of which about 65% were polyolefins (PE & PP). Figure 1.3 represents the demand of plastics resin in Malaysia in 2005 by market segments. Packaging application accounted 36 % of total resin consumption (MPMA, 2005).

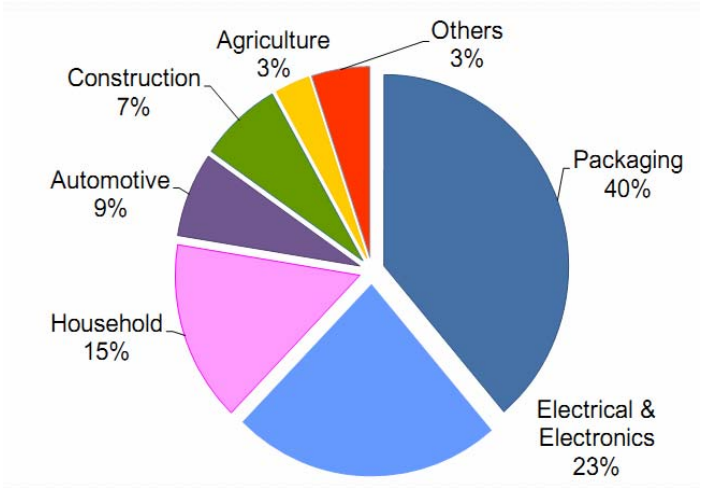


Figure 1.3 Plastics demand in Malaysia 2010 breakdown by market segments of plastics products.

Polyethylene is by far the most widely used polymeric material, accounting for 41% of the US plastic production (Osswald et al., 2006). Consumption of HDPE in United States was predicted that it would increase significantly (Lokensgard, 2004). In US, packaging accounts for over one-third of the captive use of thermoplastics, whereas construction, accounts for about half that number, and transportation account for only 4% of the total captive use of thermoplastics. On the other hand, 69% of the thermosets are used in building and construction, followed by used in transportation (Osswald and

Menges, 2003). Whereas in Europe, packaging remains the biggest end-use for plastics (40%) followed by electrical and electronic (23%), household (15%), automotive (9%), construction (7%), agriculture (3%) and others (3%) (PlasticsEurope, 2011).

Generally, most of packaging applications eventually end up as litter. Griffin (1993) reported that over 50% of the annual tonnages of all manufactured synthetic polymers are applied as packaging materials and that some 90% of this flow finishes as a component of urban garbage. The other report showed that the municipal solid waste stream in the U.S. totals nearly 160 metric tons per year and consists of about 7-11% by weight of post-consumer plastics (Andrady et al., 1993a). In 2001, plastics waste which mainly consisting of PE (above 40 wt %), PVC, PP, and poly-(ethylene terepthalate) had a total volume of 19.2 millions tons, accounting for about 8.4% of total municipal solid waste in the United States (Lei et al., 2007).

Plastic (polymers) is now being viewed as a serious worldwide environmental and health concern, especially for disposable application such as carrier and garbage bags. The increasing utilization of plastics has also caused concern for the role of plastics in environmental pollution (Lokensgard, 2004). Its character of being non-degradable is resulting in river pollution, choking in landfill, and is considered particularly undesirable and a hazard to animal life (Andrady et al., 1993a).

Some methods have been applied in order to reduce the effects of plastics on litter problem. In 1976, the Resource Conservation and Recovery Act (RCRA) promoted reuse, reduction, incineration, and recycling of materials. Recycling is a term generally reserved for post-consumer waste materials (Lokensgard, 2004). Most recycling programs accept plastics number 1 (PETE) and 2 (HDPE). The packaging of HDPE that appears in waste stream is only 25 percent of the total sales in 1993, 1,929,000 metric tons. The other products eventually find their way to landfills or incinerator (Lokensgard, 2004). However, the strategy of reduce, re-use, and recycling which have been introduced and applied widely, only overcome very small part of huge quantity of plastics waste.

1.2 PROBLEM STATEMENT

The growing environmental concern has made plastics a target of much criticism due to their lack of degradability (Albertsson et al., 1992). The large amounts of plastics ending up in the waste stream, has resulted in a trend towards manufacture and development of plastics with accelerated degradation time (Barr-Kumarakulasinghe, 1994).

Degradable polymers are designed to degrade in different ways and in different environments. An important distinction needs to be made between biodegradable plastics, i.e. those that capable of undergoing decomposition into carbon dioxide, methane, water, inorganic compounds, or biomass in which the predominant mechanism is the enzymatic action of microorganisms (bacteria, fungi, algae), and oxo-biodegradable plastics, which oxidize and embrittle in the environment and erode under the influence of ultraviolet (UV) light and heat (Excelplas, 2003).

The transition metals (Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn) could be considered for use in initiating degradation of polymers (Griffin, 1993; Osawa et al., 1979; Poyner and Cakraborty, 1993). Many studies mostly utilized cobalt-based additives for LDPE or LLDPE (Bikiaris et al., 1997; Roy et al., 2006a; Roy et al., 2007a; Roy et al., 2006b; Roy et al., 2007b; Roy et al., 2007c). The other studies utilized other transition metals, such as iron and calcium (Pablos et al., 2010) and manganese (Erlandsson et al., 1997; Khabbaz et al., 1999; Sharma et al., 2001) for LDPE. Manganese is close to cobalt in periodic table, having almost same atomic number with cobalt. Manganese is more available in the nature and cheaper than cobalt (Hartman, 1992). Moreover, most studies on degradation have focused on LDPE.

The study on effects of manganese carboxylates i.e. manganese laurate, manganese palmitate and manganese stearate on the degradation of HDPE during accelerated weathering and natural weathering under weather conditions of Gambang, Malaysia especially, and generally Peninsular Malaysia, hasn’t been existed yet. Malaysia represents tropical area. In addition, HDPE is also widely applied for post consumer products, like: packaging, plastic mulch, bottle etc. However, only few studies on degradation have focused on HDPE due to its high crystallinity, therefore it is

more difficult to degrade than one with low crystallinity. This research studies the synthesis of manganese carboxylates and the effects of manganese carboxylates on the degradation of HDPE. This study also compares the performances of manganese carboxylates i.e manganese laurate, manganese palmitate and manganese stearate on accelerating degradation of HDPE under accelerated weathering and natural weathering under weather conditions of Gambang, Malaysia.

1.3 OBJECTIVE OF RESEARCH

This research has objectives as listed below:

1. To synthesize manganese carboxylates and study their characteristics
2. To investigate the characteristics of manganese carboxylates-HDPE blends.
3. To study the effects of manganese carboxylates in accelerating degradation of HDPE under thermal treatment
4. To study the effect of manganese carboxylates on the degradation of HDPE during accelerated weathering treatment.
5. To study degradation behavior of HDPE containing manganese carboxylates during natural weathering, particularly in Gambang, Malaysia

1.4 SCOPE OF RESEARCH

The scopes of this research consist of:

1. Synthesis of manganese carboxylates.
2. Characterization of manganese carboxylates.
3. Compounding of manganese carboxylates and HDPE resins.
4. Specimen molding (injection molding)
5. Investigate the effects of manganese carboxylates on properties of HDPE
6. Thermal treatment of HDPE containing manganese carboxylates and its effect on properties of HDPE.
7. Accelerated weathering of HDPE containing manganese carboxylates and its effect on properties of HDPE.
8. Natural weathering of HDPE containing manganese carboxylates and its effect on properties of HDPE.

1.5 CONTRIBUTION OF RESEARCH

The main outputs of this research are:

1. The synthesis methods of manganese carboxylates are developed.
2. Characterization of manganese carboxylates in terms of their physical and chemical properties is obtained.
3. The pro-degradant additives for degradable HDPE are proposed and developed.
4. Degradation rate of HDPE containing manganese carboxylates during thermal treatment is obtained.
5. Degradation behaviors of HDPE containing manganese laurate under accelerated weathering and natural weathering; particularly under weather conditions of Gambang, Malaysia are well-understood.
6. Reduce lifetime of plastics waste for better quality of environment.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION TO PLASTICS

Plastics are polymeric materials with properties that are between those of elastomers and fibers. Elastomers are giant molecules possessing what is referred to as memory that they can be deformed, misshaped, and stretched, and after applied stressing force is removed, they return to their original, pre-stressed shape. Fibers posses high tensile strength and high modulus (high stress for small strains, i.e. stiffness) related to a relatively high degree of crystallinity. Plastics exhibit some flexibility and hardness and varying degrees of crystallinity (Carraher Jr., 2003).

Polymers are very large molecules (macromolecules) that are comprised or built up of smaller units or monomers. This monomer term is also used to indicate the basic chemical compound from which the polymer is polymerized. For example, the polymer polyethylene is produced from the monomer ethylene. It is usual to represent such a polymer in terms of its chemical repeat unit, as follows:

$$-(CH_2\text{-}CH_2)_n-$$

where n, which is the number of repeating units, can be large (ASM International, 2003; Painter and Coleman, 1997).

Polymers can be placed into thermoplastic, thermoset, or elastomer category. Thermoplastics are those polymers that solidify as they cooled no longer allowing the long molecules to move freely. When heated, these materials regain the ability to flow, as the molecules are able to slide past each other with ease. Thermosetting polymers solidify by being chemically cured. Here, the long macromolecules cross-link with each other during cure, resulting in a network of molecules that cannot slide past each other.

The formation of these networks causes the materials to lose the ability to flow even after reheating. Compared to thermosets, elastomers are only lightly cross-linked which permits almost full extension of the molecules. However, the links across the molecules hinder them from sliding past each other, making even large deformations reversible. They are very soft and very compliant elastic materials (Osswald and Menges, 2003).

Thermoplastic polymers are divided into two classes: amorphous and semi-crystalline polymers. The most common semi-crystalline thermoplastics are high density polyethylene, low density polyethylene, polypropylene, polytetrafluoroethylene, polyamide (Carraher Jr., 2003; Osswald and Menges, 2003). Amorphous polymers form large group of materials, including glassy, brittle polymers (such as polystyrene (PS), polymethyl methacrylate (PMMA), styrene acrylonitrile (SAN), and cyclic olefin copolymer (COC)) and ductile polymers (such as polyvinyl chloride (PVC) and polycarbonate (PC)). The characteristic that such polymers have in common is their "amorphous" structure, which means that they do not exhibit any crystalline structure in X-ray or electron scattering experiments (Michler, 2008)

2.2 POLYETHYLENE

Polyethylene (PE) (sometimes known as polythene) was discovered in 1933 by Reginald Gibson and Eric Fawcett at the British industrial giant. Imperial Chemical Industries (ICI) (Vasile and Pascu, 2005). In its simplest form a polyethylene molecule consists of a long backbone of an even number of covalently linked carbon atoms with a pair of hydrogen atoms attached to each carbon; chain ends are terminated by methyl groups. This structure is shown schematically in Figure 2.1 (Peacock, 2000), and the simple molecular structure is presented in Figure 2.2 (ASM International, 2003).

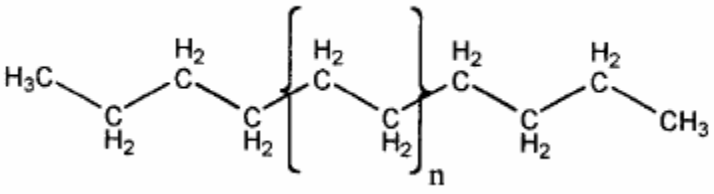


Figure 2.1 Chemical structure of polyethylene

Chemically pure polyethylene resins consist of alkanes with the formula $C_{2n}H_{4n+2}$, where n is the degree of polymerization, i.e. the number of ethylene monomers polymerized to form the chain. Unlike conventional organic materials, polyethylene does not consist of identical molecules. Polyethylene resins comprise chains with a range of backbone lengths. Typically the degree of polymerization is well in excess of 100 and can be as high as 250,000 or more, equating to molecular weights varying from 1400 to more than 3,500,000. Low molecular weight polyethylenes (oligomers) with a degree of polymerization between 8 and 100 are waxy solids that do not possess the properties generally associated with a plastic. When the degree of polymerization is less than 8, alkanes are gases or liquids at ordinary temperatures and pressures. Polyethylene molecules can be branched to various degrees and contain small amounts of unsaturation (Peacock, 2000).

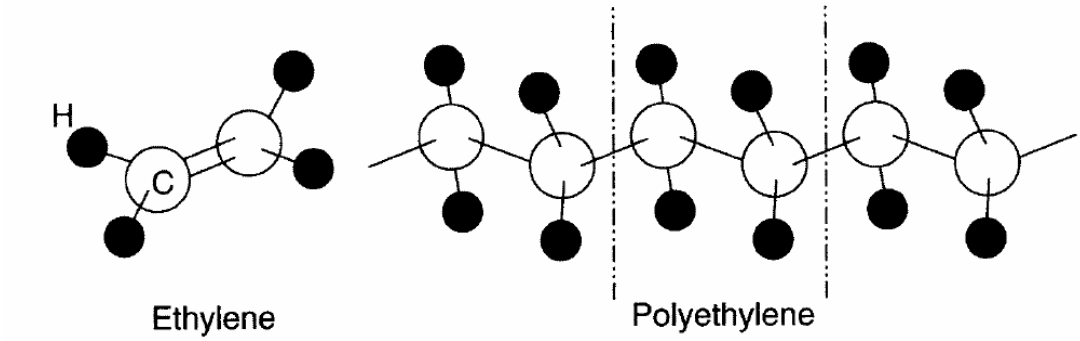


Figure 2.2 Molecular structure of polyethylene

Polyethylene is synthesized in several ways and resulting in different types of polyethylene. The branched polyethylene is called low density, high pressure polyethylene because of high pressure usually employed for its production; and because of the presence of the branches, the chains are not able to closely pack, leaving voids and subsequently producing a material that has a lower density in comparison to low-branched polyethylene. The other type of polyethylene is synthesized at much lower pressure and temperatures. This polyethylene has fewer branches and a higher softener temperature (above 100°C) (Carraher Jr., 2003).